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SOL-GEL METHOD IN OXIDE MATERIAL TECHNOLOGY

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The principles of producing highly disperse powders of oxide materials, including complex compositions, using the sol-gel method are considered. Various compounds (polyacrylic acid, polyacrylamide, polyvinyl alcohol) are used as the gel-forming agents in true and colloid solutions. When powders are produced by the sol-gel method, the temperature of synthesis of complex compounds decreases by 150–200°C and the particles in this case have nanosizes.

Intensification of technological processes in metallurgy, power, chemical, aircraft, and automobile sectors, as well as development of radioelectronics, nuclear power, spacecraft engineering, etc., call for continuous development of new kinds of materials, including ceramics with special properties. Oxide materials are among the most promising. They have found extensive applications in fields of engineering requiring heat resistance, increased strength, hardness, and corrosion resistance. These materials play an important role in industrial sectors requiring materials with high electric, optical, and mechanical parameters.

The main purpose in the development of new kinds of ceramics is ensuring their stable properties, which increases their reliability in different conditions, including extreme conditions.

To produce high-quality ceramics, manufacturers lately often use sublimated non-aggregated powders with a particular shape of particles, usually approaching a spherical shape, and high activity in sintering.

Ceramics technology frequently uses the method of coprecipitation of salts or hydroxides from solutions to produce sintering-active, homogenous, and highly disperse (particles size below 1 μm) powders. Numerous studies in this field made it possible to formulate the main principles of this technology of powder preparation, determine precipitation procedures and sequence of component mixing, and to identify numerous factors influencing the quality of the end product. However, big difficulties in implementing the coprecipitation method are related to the necessity of using substantial quantities of ammonium (the main component for transfor-

mation of salts into hydroxides) and acetone, which ensures faster drying of powder and avoidance of disaggregation. The environmental purity of the process of production of highly disperse ceramic powders by the coprecipitation method is far from perfect.

At the moment numerous domestic and especially foreign researchers (Japan, Germany, etc.) are developing methods for producing finely disperse monofraction powders using sol-gel technology (Japan Patent Applications Nos. 61-22917, 62-226816, 62-233018) [1–3]. Production of disperse particles by this method is implemented by means of hydrolysis of respective compounds of elements making part of the target oxide composite. As a result of the reaction and subsequent condensation, particles consisting of oxides and hydroxides are obtained. The composition of particles is determined by the conditions of hydrolysis and the nature of initial compounds. The homogeneity of component distribution depends on the selection of initial compounds and the conditions of hydrolysis reactions. A specific feature of the sol-gel method is the fact that fragments of future oxides, not only simple oxides, but of complex compositions as well are formed already in the gel phase, which reduces diffusion barriers in solid-phase sintering to a minimum and, naturally, decreases the time of synthesis. At the same time a homogeneous distribution of components on the molecular level is ensured.

The Department of Chemical Engineering of Ceramics and Refractories at D. I. Mendeleev Russian Chemical Engineering University starting with 1990-s has been researching and upgrading another variant of sol-gel technology, whose fundamental principle consists in producing a high-molecular polymer gel and distributing a homogenous true solution of one or several components in this gel. The dried xerogel is

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TABLE 1

Sample	Content of PAA, %	Ratio of monoclinic to cubic phases, %	Particles size, μm
1	30	25 : 75	60 – 120
2	60	15 : 85	30 – 80
3	90	5 : 95	< 1

calcined at relatively low temperatures (from 600 to 1200°C depending on the type and nature of oxide) converting a porous mixture into friable non-agglomerated powder. This variant of the sol-gel method ensures production of monodisperse powders of simple or complex metal oxides with particle size below 1 μm and significantly smaller (nanoparticles).

The organic reactant used in the development of technology for producing ultradisperse powders of zirconium dioxide stabilized by yttrium oxide was polyacrylic acid (PAA). The preparation of aqueous solution and the process of gel formation are crucial phases in sol-gel technology, since the properties of the future product of synthesis are laid in these phases. Since PAA coagulates at pH below 5 and above 7, in preparing an aqueous solution of zirconium and yttrium nitrates with pH not exceeding 1.5, ammonium nitrate was introduced into the system in an amount ensuring an increase in pH to 5 – 6.

Concentration of PAA has an effect not only on the gel formation process, but on the properties of powder calcined at 1200°C. A steady gel not separating with time was obtained with a ratio of PAA to water at least 3 : 1. The size of powder particles significantly decreases, as a concentration of PAA increases (Table 1). An increase in the quantity of PAA in a solution facilitates transformation of the monoclinic phase of ZrO_2 into a cubic solid solution. The data in Table 1 are given for solutions with constant concentrations of zirconium nitrate (110 g/liter) and stabilizing additive (15%).

In contrast to the gel-forming agent, an increase in concentration of the main component in a range from 25 to 225 g/liter has virtually no effect on the particle size, nor on the phase composition (Table 2).

The quantity of the stabilizing additive as well has no effect on the behavior of gel in calcination. According to the x-ray phase analysis and petrography data, zirconium dioxide is mainly formed in the form of a solid solution of the cubic modification with particle size below 1 μm , regardless of the quantity of yttrium oxide (Table 3).

According to data in [2, 3], the temperature of transition from one phase of zirconium dioxide to the other decreases, as the particle size gets smaller. It is also known that ultrafine particles of zirconium dioxide, which make the greatest contribution to the total elastic stresses, sometimes have a cubic phase. These facts are corroborated in our research: the cubic modification of the solid solution of zirconium dioxide with

TABLE 2

Sample	Concentration* of $\text{ZrO}(\text{NO}_3)_2$, g/liter	Ratio of monoclinic to cubic phases, %	Particles size, μm
1	27.6	0 : 100	< 1
2	55.5	0 : 100	1
3	82.0	5 : 95	1
4	110.0	5 : 95	< 1
5	150.0	7 : 93	1
6	200.0	2 : 98	< 1
7	225.0	5 : 95	< 1

* In all cases content of PAA 90 g/liter, Y_2O_3 — 15%.

TABLE 3

Sample	Concentration* of $\text{ZrO}(\text{NO}_3)_2$, g/liter	Content of Y_2O_3 in solution, g/liter*	Ratio of monoclinic to cubic phases, %
1	110	5.14	0 : 100
2	110	7.7	0 : 100
3	110	11.9	7** : 93
4	110	15.5	5 : 95
5	225	4	7 : 93
6	225	6	5 : 95
7	225	7	2 : 98
8	225	10	2 : 98
9	225	11	7 : 93

* Concentration of PAA 90 g/liter.

** Including 4% tetragonal phase.

yttrium oxide is formed at 1200°C, whereas normally such modification emerges at higher temperatures.

Highly disperse powders of stabilized zirconium dioxide were used to make gaskets used in firing of corundum cases for integral circuits. The service life of such gaskets was significantly extended compared with standard industrial ones, which was due to increased adhesion resistance with respect to material fired. The mechanism of improvement of service parameters of gaskets consists in higher dispersion of zirconium dioxide particles, compared with industrially made analogs, accordingly, these particles are distributed over a larger surface area of the main component in the gasket composition and neutralize its chemical activity and capacity to react with corundum cases fired.

One of application areas for highly disperse powders is introducing them as very small additives into known compositions or replacing some additives obtained by traditional methods. A possibility was tested of replacing a highly disperse additive of the $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$ system used in "Coral-2" ceramics (USSR Inventor's Certif. No. 1453814) and produced by precipitation of respective salts by a sol-gel powder of the same system. Besides, a small quantity of Cr_2O_3 was added to the known composition [4].

Gels of the specified system were obtained by pouring aqueous solutions of respective metal salts to PAA, which

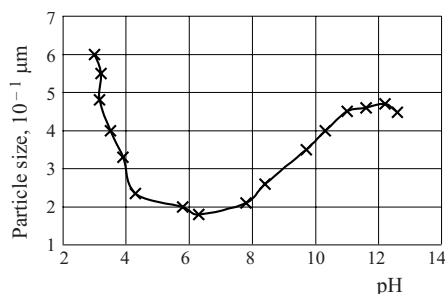


Fig. 1. The effect of pH of the medium on the size of powder particles.

was the main component in gel formation. Dissolution was carried out in a wide temperature range from 10 to 100°C, the optimum interval was between 18 and 25°C. Going beneath the lower limit complicates the technological process, and exceeding the upper limit leads to formation of a suspension in the solution and precipitation of a white sediment in the form of flakes.

The pH of the medium has a significant effect on the steadiness of gel and the size of powder particles obtained after its calcination. With pH = 2 gel formation is impeded due to coagulation of PAA, and increasing pH to 6–7 raises the stability of gel. Gel formation in an alkaline medium (pH = 8–10) proceeds very fast, consequently, gel does not absorb all components of the solution, which disturbs their ratio in the powder.

The dependence of particle size on pH is extremal (Fig. 1), the smallest size (0.2–0.5 μm) being registered at pH = 6–7. The ratio of the solution volumes of salts and the gel-forming agent as well affects the size of powder particles. To obtain the smallest particles (0.1–0.2 μm) in the $\text{Al}_2\text{O}_3\text{--ZrO}_3\text{--CrO}_3$ system, this ratio has to be 1 : 6 and in the $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--Y}_2\text{O}_3\text{--Cr}_2\text{O}_3$ system it should be 1 : 20 or less.

Calcination of xerogels obtained at a temperature of 1200°C (exposure 2 h) ensures 100% conversion of aluminum oxide from the γ -modification to the α -modification. Zirconium dioxide is present in the tetragonal form as a cubic solution of yttrium oxide in zirconium dioxide. The powder consists of individual easily disintegrating aggregates of the fibrous structure, which unite crystals sized 0.1–0.3 μm .

The success of chemical methods, including the sol-gel process suggests that they can be extended to extensive production not just of simple one-component materials, but mainly to synthesis of multicomponent systems, since a high degree of homogeneity of resulting mixtures compares very favorably with such traditional techniques as, for instance, mechanical mixing.

The optimum electric and mechanical properties of piezoceramics, to which ZTL belongs, are usually manifested in materials with the most perfect structure and maximum homogeneity of chemical composition.

To synthesize ZTL powders, water-soluble inorganic salts of respective components were selected: titanyl sulfate, zirconyl nitrate, lead nitrate, and polyacrylamide as the organic reactant.

Since the procedure of xerogel calcination (temperature and exposure duration) has a significant effect on the phase composition and dispersion of powders, several variants were selected based on published data [5, 6]: temperatures of 800, 900, and 1000°C with 1-hour exposure and 700, 800, and 900°C with 3-h exposure.

According to the data of x-ray phase analysis, petrography, and electron microscopy, synthesis at 800°C (1 h) is 60% completed, the particle size is not more than 1 μm , whereas 40% is comprised by titanium, zirconium, and lead oxides with particles of the same size. At 900°C (1 h) synthesis of ZTL is virtually completed, there is just a small excess (about 1.5%) of lead oxide, the particle size varies from 1 to 2 μm . An increase in temperature to 1000°C with the same exposure leads to recrystallization of the phase (with 100% synthesis of ZTL), the particle size ranges from 2 to 4 μm , the crystals have a rounded shape. A three-hour exposure at 700°C yields 60% of fully synthesized ZTL and 35% of a phase close to ZTL, whereas 5% is taken by lead oxide; the particle size is below 1 μm . When temperature is raised to 800°C, synthesis is virtually completed, there is a slight amount of excessive lead oxide (up to 2%) distributed over the periphery of ZTL, the crystal size is up to 2 μm . Thus, it is possible to obtain a fully synthesized product already at 800°C, whereas usually it is synthesized in special containers at 910°C [7].

In producing highly disperse powders of aluminomagnesium spinel, in addition to PAA and polyacrylamide, other water-soluble organic reactants were used for gelation, for instance polyvinyl alcohol [8].

The aluminum-bearing salts selected for the studies were chloride and nitrate crystal hydrates as the most available and relatively inexpensive components. Magnesium-bearing salts were also represented by crystal hydrates of chloride and nitrate and also citrate and acetate, whose effect on gel formation and synthesis of spinel was investigated for the purpose of improving environmental efficiency, since the latter salts in decomposition release only water vapor and carbon dioxide.

Twelve compositions were investigated, which were selected with the view of a maximum number of possible combinations of salts with anions of like and opposite signs.

The components ratios (converted to Mg and Al oxides) were selected to encompass a wide range: from a stoichiometric composition (for all possible combinations) to a ratio of 1 : 10, which is equivalent to 90% deficit of MgO compared with its content in spinel. Moreover, compositions with 50% deficit of MgO were investigated for combinations with like anions (Table 4).

Spinel was synthesized at temperatures of 800, 1300, and 1600°C for 1 h. The bottom limit was chosen based on the

TABLE 4

Combination of salts	Mixtures	Experiments* with deficit of MgO, %		
		0	50	90
AlCl ₃ – MgCl ₂	1-I	+	+	+
AlCl ₃ – Mg(NO ₃) ₂	1-II	+	–	+
AlCl ₃ – Mg ₃ (C ₆ H ₅ O ₇) ₂	1-III	+	–	+
AlCl ₃ – Mg(CH ₃ COO) ₂	1-IV	+	–	+
Al(NO ₃) ₃ – MgCl ₂	2-I	+	–	+
Al(NO ₃) ₃ – Mg(NO ₃) ₂	2-II	+	+	+
Al(NO ₃) ₃ – Mg ₃ (C ₆ H ₅ O ₇) ₂	2-III	+	–	+
Al(NO ₃) ₃ – Mg(CH ₃ COO) ₂	2-IV	+	–	–

* +) experiment was carried out; –) experiment was not carried out.

results of previous studies, which demonstrated a possibility of production of spinel and formation of solid solutions of aluminum oxides in spinel at this temperature. Since many researchers indicate that spinel is synthesized fully enough at 1300°C, we selected this temperature for synthesis. Finally, synthesis at 1600°C was planned, since, according to some data, this temperature may cause decomposition of solid solutions.

In virtually all combination of salts investigated, spinel formation, or more precisely, transition of spinel from the amorphous state into a crystalline one is registered at about 800°C.

In our opinion, formation of spinel at the molecular level occurs already in true solution, furthermore, the system in this case is virtually equilibrium, and processes are determined by thermodynamics. The possibility of such reaction is corroborated by the thermal effect value (although low) of this reaction ($\Delta H_{298}^0 = -19.01$ kJ/mole). Since kinetic conditions in solutions are favorable, the formation of a new chemical compound, in our case spinel, is quite probable. Evidently, this compound up to a certain temperature exists

in the amorphous (or at least x-ray-amorphous) state. The process of recrystallization starts at a temperature of 700–800°C and only some compositions crystallize at 840–870°C (those based on stoichiometric magnesium chloride and magnesium nitrate with ratio 1 : 10).

The diffraction patterns of xerogels calcined at 800°C corroborate the formation of spinel at this temperature (Table 5). The effect of magnesium salt anions on the phase composition of stoichiometric powders calcined at 800°C is quite significant. Thus, whereas only one spinel phase typically emerges in magnesium nitrate and citrate, another phase (MgO) is registered in magnesium chloride, and as for acetate, in addition to spinel, θ - and even α -Al₂O₃ are registered.

The absence of other phases apart from spinel in mixtures based on magnesium nitrate and citrate (with aluminum nitrate) suggests that favorable conditions for the formation of stoichiometric spinel are created in the system of these anions. Calcination of these mixtures at 1300°C disturbs the stoichiometric ratio, accordingly, Al₂O₃ emerges as α -form and in the case of citrate as θ -form as well.

Magnesium acetate creates an environment facilitating early crystallization of spinel (of all compositions it has the lowest temperature of the exothermic effect of crystallization), however, it does not ensure the production of stoichiometric spinel even with the ratio MgO : Al₂O₃ = 1 : 1. Aluminum oxides emerging as α - and θ -forms after calcination of xerogel at 800°C is preserved as well after calcination at temperatures 1300 and 1600°C.

Another mechanism of phase formation is implemented when using magnesium chloride as the magnesium-bearing component. With a component ratio corresponding to a stoichiometric composition of spinel, heating at 800°C leads to the formation of free magnesium oxide, which is preserved after calcination at 1300 and 1600°C. In other words, part of MgO is not incorporated in the spinel lattice and per-

TABLE 5

System	Ratio MgO : Al ₂ O ₃	Phase composition after calcination at temperature, °C			Spinel crystallization temperature (DTA data), °C
		800	1300	1600	
Al(NO ₃) ₃ – MgCl ₂	1 : 1		Spinel, MgO		840 – 870
	1 : 10	Spinel	Spinel, α -Al ₂ O ₃		730 – 750
Al(NO ₃) ₃ – Mg(NO ₃) ₂	1 : 1	Spinel	Spinel, α -Al ₂ O ₃	Spinel	765 – 835
		Spinel*			
	1 : 2	The same	The same	Spinel, α -Al ₂ O ₃	755 – 800
		The same*			
	1 : 10	–	"	The same	840 – 875
		Spinel			
		The same	Spinel, α -Al ₂ O ₃ , θ -Al ₂ O ₃		750 – 790
Al(NO ₃) ₃ – Mg ₃ (C ₆ H ₅ O ₇) ₂	1 : 1	The same	Spinel, α -Al ₂ O ₃ , θ -Al ₂ O ₃		825 – 850
	1 : 10	"	The same		
Al(NO ₃) ₃ – Mg(CH ₃ COO) ₂	1 : 1	Spinel, α -Al ₂ O ₃ , θ -Al ₂ O ₃		Spinel, θ -Al ₂ O ₃	690 – 730
	1 : 10	Spinel, γ -Al ₂ O ₃	Spinel, α -Al ₂ O ₃		815 – 860

* Exposure at temperature 800°C for 3 h.

sists in free form, whereas aluminum oxide becomes incorporated in the spinel lattice and forms a solid solution. To obtain a single-phase material, it is possible to organize a partial removal of magnesium oxide from the mixture to correlate with the stoichiometric composition. It was established in previous studies that decreasing magnesium oxide by 90% compared to a stoichiometric composition after calcination at 800°C makes it possible to obtain a single-phase material. This statement was corroborated on mixtures containing magnesium chloride, nitrate and citrate, which after calcination at 800°C did not have any other phase apart from spinel. Crystallization of spinel from powder based on magnesium nitrate occurs only after 3-hour exposure at 800°C, whereas after a 1-h exposure the powder remains x-ray-amorphous. This is comprehensible considering that the spinel crystallization temperature for xerogels of this composition is the highest among all combinations considered, namely, 840 – 875°C.

A decrease in a content of magnesium-bearing component in xerogel based on magnesium acetate results in the formation of another phase, namely, $\gamma\text{-Al}_2\text{O}_3$. Apparently, a 90%-deficit of MgO is too substantial for the production of a single-phase material.

Heating nonstoichiometric powders to higher temperatures causes disintegration of solid solutions and formation in addition to spinel (or more precisely, in addition to the solid solution in spinel) of one or several more Al_2O_3 phases in the form of θ - or α -modifications.

A special place among highly disperse powders that can be produced by the sol-gel method is taken by mullite and forsterite containing a siliceous component. A limited number of soluble silicon-bearing salts and their high cost determined the use of highly disperse amorphous silicon dioxide powder known as “silica filler” as the initial component. Silica filler forms a colloid solution in water, which has sufficient resistance to aggregation and sedimentation. The second components for production of mullite powders were crystal hydrates of aluminum compounds: chloride, nitrate, and sulfate, and for forsterite powders, magnesium chloride, nitrate, sulfate, acetate, and citrate.

It was found in synthesis of mullite powders [9, 10] that the form of the initial aluminum compound in sol-gel technology has a significant effect on the completion and course of the reaction, the starting temperature, and the shape of crystals. The completion of mullite formation, furthermore, significantly depends on the temperature of xerogel calcination. Thus, the beginning of mullite formation in xerogel based on aluminum chloride, according to DTA data, was registered at 500°C. The emerging crystals are hard to identify by x-ray analysis due to their small sizes, and the formation of mullite is registered on the diffraction pattern only starting with 900°C. Starting with 800°C, absorption bands typical of mullite are seen in the IR spectra, and fiber-shaped mullite crystals are petrographically identified in substantial quantities (80%), their major part being in transitional forms.

Only starting with 1000°C, the amount of well crystallized mullite exceeds 80%.

The formation of the mullite phase in xerogel based on aluminum sulfate is analogous to aluminum chloride, the only difference being the shape of crystals resembling scales.

Xerogel based on aluminum nitrate due to a specific effect of the anions does not form mullite at low temperatures, therefore, silica filler crystallizes at a temperature of 800 – 900°C transforming into α -tridimite, which impedes mullite formation. The amount of mullite becomes perceptible only at 1100°C (about 15% round-shaped crystals). All xerogels after calcination in addition to mullite contain aluminum oxide in some form, which is due to part of silica passing into the solid solution or formation of a compound of the type 1 : 1.

Synthesis of forsterite from xerogel based on magnesium nitrate and silica filler is less intense, since the magnesium salt is hard to decompose and even at 800°C, according to petrographic data, 5 – 7% non-decomposed nitrate remains. The rest is comprised by solid solutions with the forsterite lattice. An increase in temperature to 1200°C raises the amount of finely dispersed forsterite phase, at the same time excessive SiO_2 up to 10% is formed.

In xerogel based on magnesium sulfate and silica filler, the amount of fine (below 1 μm) forsterite crystals reaches 70 – 75%, besides, a substantial quantity (about 15%) of enstatite phase is formed. At 1200°C the amount of forsterite and forms transitional to forsterite reaches 100%.

According to x-ray phase analysis and petrography data, the formation of 80% forsterite with crystals sized up to 2 μm and a strongly deformed lattice in calcination of xerogel based on magnesium acetate is registered already at 600°C. Forsterite formation is less intense in xerogel based on magnesium citrate. Thus, at 600°C only 50% forsterite with a distorted crystalline lattice emerges, the rest is taken by intermediate phases. Even raising temperature to 1200°C increases the yield of forsterite only up to 85%, of which only 25% constitutes well formed crystals. The remaining 15% is taken by SiO_2 in fixed and in free states.

Thus, an assumption is made that reactions between components in mixing solutions occur due to electrostatic attraction of magnesium cations to the negatively charged surface of the silica particles, which proceeds more completely in an alkaline medium. Since crystal hydrates of acetate, sulfate, and chloride provide for a more alkaline medium (pH of the solutions is 7.54, 6.62, and 5.90, respectively) than crystal hydrates of citrate and nitrate (pH = 4.50 and 2.03), the formation of forsterite in them is more intense and occurs at lower temperatures.

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